

STUDIES ON OVERVOLTAGE

XIII---Decay of Cathode Potential in Still and Stirred Solutions Saturated With Hydrogen or With Nitrogen.

XIV---A Study of Hydrogen Decomposition Potentials Under Various Conditions in Acid Solutions at Platinized Platinum Electrodes.

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
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STUDIES ON OVERVOLTAGE

Electrolysis of Carbonic Acid in Acid and Alkaline
Solutions with Hydrogen as Working
Electrode

By A. R. J. VAN DER PLOEGH, Laboratory of Physical
Chemistry, University of Leiden, The Netherlands



STUDIES ON OVERVOLTAGE. XIII.
DECAY OF CATHODE POTENTIAL IN STILL AND STIRRED
SOLUTIONS SATURATED WITH HYDROGEN OR
WITH NITROGEN*

By A. L. FERGUSON** AND MYRON B. TOWNS***

ABSTRACT

This is a continuation of studies on overvoltage. Attention is confined here to the natural decay on open circuit of cathode potentials at platinized platinum electrodes. Four factors were altered: first, a still solution saturated with hydrogen was used; second, a stirred solution saturated with hydrogen; third, a still solution saturated with nitrogen; and fourth, a stirred solution saturated with nitrogen. The object in each case was to produce a condition that would influence the rate of diffusion of active material away from the electrode-solution interface. Previous experiments had indicated that cathode polarization potentials are determined by the activity of atomic hydrogen and hydrogen ions at the electrode-solution interface. The work was designed to provide information on this theory. All of the data obtained support the theory.

INTRODUCTION

The last two papers of this series, Part XI¹ and Part XII,² reported experiments which were designed to throw light upon the mechanism of electrode potentials and overvoltage. On the basis of evidence presented in Part XI¹ and also earlier observations, the senior author proposed: (1) that the back potential at a platinized platinum electrode throughout the whole range of polarization including overvoltage, in acid solution, is due to the discharge of an active material at the electrode surface; (2) that the concentration of this active material, and, therefore, the cathode potential, is determined by the difference in rate of formation and rate of removal at the interface; and (3) that the primary factor involved in the removal is diffusion. On open circuit the decrease in this back potential is due to the removal of the active material from the interface largely by diffusion. Since, however, the

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¹ A. L. Ferguson and H. Bandes, *Trans. Electrochem. Soc.* **81**, 273 (1942).

² A. L. Ferguson and H. Bandes, *Trans. Electrochem. Soc.* **81**, 291 (1942).

*Address of the Secretary of the Society: Columbia University, New York City.

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potential of an electrode is determined not only by the effective concentration of electrode material on the electrode side of the interface but also by the activity of the ions of the electrode material on the solution side of the interface, it is necessary to consider factors that might cause the activity of the ions in a layer a few molecules thick at the metal-solution interface to change and differ from their activity in the body of the solution. It is, of course, the ion activity in this extremely thin layer that determines the electrode potential, rather than the activity in the body of the solution. This factor, *i.e.*, the activity of ions at the interface, probably becomes increasingly important as the current density increases. Ions will always be discharged at a greater rate than they are replaced by current conduction. In the case of hydrogen ions they are probably highly hydrated and when discharged leave their water of hydration at the interface. Also, since the electrode is wet by water, it is highly probable that the electrode is covered with a layer of absorbed, oriented water molecules from which more 0.673 v. against a platinized platinum electrode in 2 *N* sulfuric acid or less of the electrolyte may be "salted out."

The evidence presented in Part XII² supported these conclusions. It was shown that the decay of both anode and cathode overvoltage was logarithmic with time, as would be expected if the decay of overvoltage were due to diffusion processes at the electrode-electrolyte interface.

If the back potential at the cathode preceding and during electrolysis is due to the presence of an active material liberated by the current, then the rate of decay on open circuit should be greater in stirred solutions than in still solutions; likewise, the rate should be greater in solutions saturated with nitrogen than in solutions saturated with hydrogen, and even greater when these nitrogen-saturated solutions are stirred. The present paper is concerned with a study of the decay of cathode potential under various carefully controlled conditions in order to test these predictions.

APPARATUS

The apparatus used was fundamentally the same as that described in an earlier paper.¹ Only the cell and the amplifier were significantly different. The three-chambered cell used in this research is shown in Fig. 1. The cathode, middle, and anode chambers are designated, respectively, by *K*, *M*, and *A*. Each chamber was closed with a rubber stopper carrying a gas inlet tube, *I*, and exit tube, *T*, and was equipped with a gas trap containing 2 *N* sulfuric acid. The cathode was platinized platinum, 1 cm. on edge and coated with paraffin on the back. The electrolyte used throughout the cell was 2 *N* sulfuric acid. The filter paper plugs, *C*, were inserted to minimize diffusion from one part of the cell to another.

The cell was polarized by a constant current obtained from two heavy-duty 45 v. dry cells in series with a resistance of suitable size. The exact current used was determined by measuring the fall of potential across a standard resistance in the charging circuit.

The anode and cathode reference electrodes had a potential of + 0.673 v. against a platinized platinum electrode in 2 *N* sulfuric acid

saturated with hydrogen at 25° C. Hereafter all potentials will be given with reference to the platinized platinum electrode as zero.

The d.c. amplifier used is shown in Fig. 2. It differs from the one described by Ferguson and Kleinhessel³ mainly in the following points:

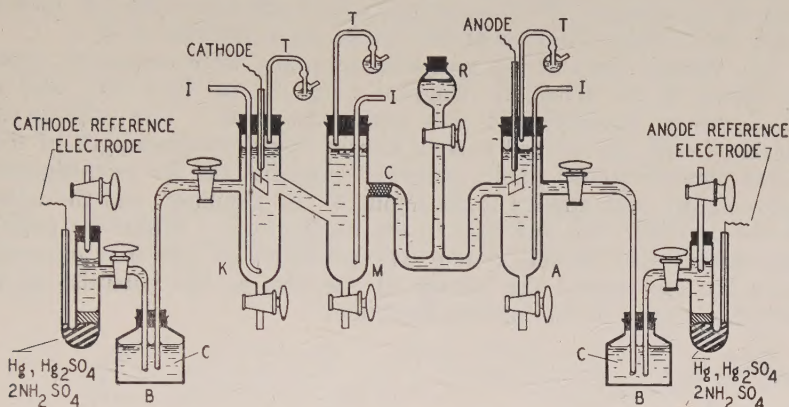


FIG. 1. Diagram of cell.

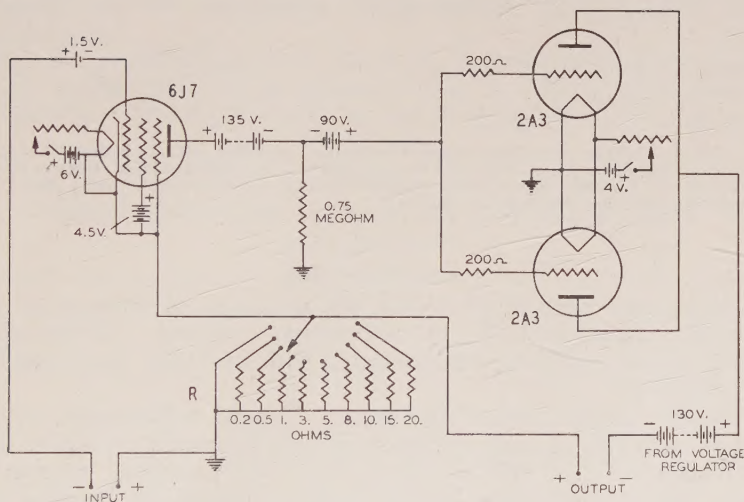


FIG. 2. Amplifier.

(1) a 6J-7 tube was used in the first stage; (2) two 2A-3 tubes in parallel were used in the second stage to increase the power output of the instrument; (3) the plate supply for the second stage was obtained from a modification of the RCA Model TMV-118-B voltage regulator described earlier¹; (4) the sensitivity of the amplifier was varied by

³ A. L. Ferguson and S. Kleinhessel, *J. Phys. Chem.* **42**, 172-190 (1938).

making use of the degeneration principle. Ten different amplifications were obtained by means of ten resistors. The proper resistor to produce the desired amplification was put in series with the positive input lead and the output was returned to a movable contact on the cathode side of the resistor. The overall gain of the amplifier with this arrangement was a linear function of the size of the resistance⁴ at R .

The various units of the apparatus assembly were connected exactly as shown in the schematic diagram (Fig. 2) of Part XI,¹ and the procedure of measurement was much the same. The cathode was polarized with the desired current density for a known length of time. After measuring the stable, polarized potential on the potentiometer, this potential was applied to the input of the amplifier, and the output of the amplifier was switched to the oscillograph. When the polarizing current was broken, a line was produced on the film extending from the top toward the bottom of the film as the potential of the cathode decayed in the positive direction.

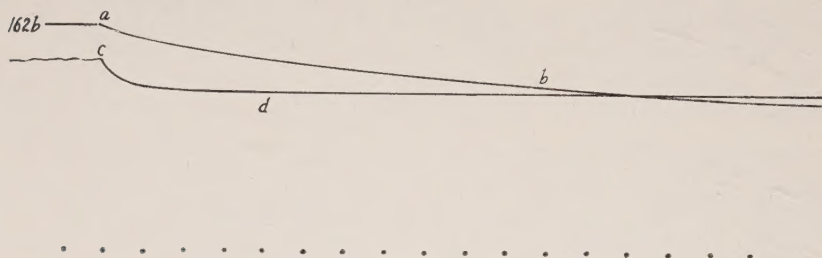


FIG. 3. Cathode overvoltage decay in solutions saturated with hydrogen. Charged potential for still solution (top line) was -0.024 v.; for stirred solution (bottom line), -0.006 v. For both lines, current density was 0.454 milliamp./cm.², timing dots at 5 sec. intervals, and amplification system 1.

EXPERIMENTAL

Oscillograms were taken of the *natural* decay of overvoltage of a polarized cathode in both *still* and *stirred* solutions. In one set of experiments the solution was *saturated* with *hydrogen* and in another, with *nitrogen*.

Solutions Saturated with Hydrogen. Typical oscillograms of overvoltage decay in *still* solutions saturated with hydrogen are shown in the top lines of Fig. 3 and 4. At point *a* the polarizing current was broken by the interrupter and the cathode overvoltage decayed along *ab*. Several oscillograms of this nature were taken following polarization with currents from 0.224 to 7.66 milliamp.

In earlier work^{1, 2, 3} it has been demonstrated that no part of the overvoltage on a number of metals up to current densities as high as 30 milliamp. is due to an IR drop across a film at the electrode-solution interface. This is further verified by these oscillograms since

⁴ The ten systems of amplification used had the following sensitivities expressed as millivolts input per milliamper change in output:

System	1	2	3	4	5	6	7	8	9	10
$R(\text{ohms})$	0	0.2	0.5	1.0	3.0	5.0	8.0	10.0	15.0	20.0
Sensitivity	0.51	0.76	1.05	1.57	3.6	5.4	8.6	10.7	15.8	20.8

in no case was there an initial vertical drop in the decay curve that would be required if some of the measured overvoltage were due to the fall of potential across a pure resistance. Also, in no case did the potential of the cathode decay to the reversible value during the exposed two-thirds of the film drum, about one and one-half minutes.

Table I gives the stable cathode potentials corresponding to each

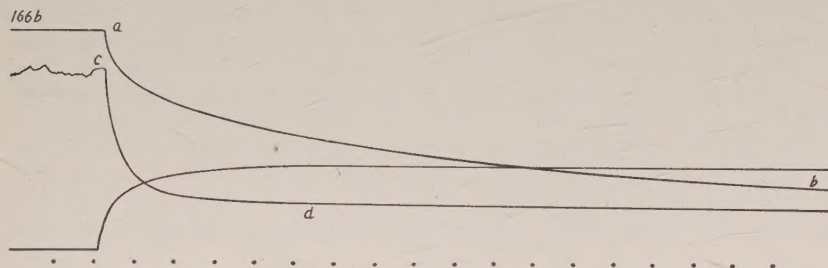


FIG. 4. Cathode overvoltage decay in solutions saturated with hydrogen. Charged potential for still solutions (top line) was -0.040 v.; for stirred solutions (middle line), -0.026 v. For both lines, current density was 3.54 milliamp./cm.², timing dots at 5 sec. intervals, and amplification system 1.

current and the results of measurements made by means of an accurate comparator on the oscillograms during the first thirty seconds of the natural decay.

The data in columns 3, 5, 7, and 9 are plotted against the logarithm of time in the upper set of curves of Fig. 5. These curves and the tabulated data show clearly that the rate of decay increased with an in-

TABLE I
Cathode Overvoltage Decay in Still Solutions Saturated with Hydrogen

Current in milliamp.	Cathode Potential in millivolt	Total Decay of Overvoltage after							
		5 Sec.		10 Sec.		20 Sec.		30 Sec.	
		mv.	%	mv.	%	mv.	%	mv.	%
0.224	-19	1.7	8.9	2.2	11.6	3.9	20.5	5.1	26.8
0.454	-24	2.6	10.8	3.7	15.4	6.2	25.9	7.8	32.5
1.30	-33	6.0	18.2	7.4	22.4	10.7	32.4	13.0	39.4
3.54	-40	10.6	26.5	13.6	34.0	17.7	44.3	20.3	50.7
7.66	-47	17.7	37.7	21.5	45.7	25.9	55.1	29.0	61.7

crease in the current used during the preceding polarization. It is, of course, not the currents that are of primary interest here, but rather the resulting cathode potentials, or overvoltages. These are stable potentials for the corresponding currents and, according to the theory proposed earlier, are due to some definite concentration of the same material, *i.e.*, active hydrogen at the interface. Naturally, if this is the case, the rate of disappearance, and thus the rate of decay of cathode

potential on open circuit, will be greater the higher its concentration; or in other words, the higher the overvoltage. Also, if the disappearance is due to diffusion into the solution, the resulting overvoltage will be proportional to the logarithms of the time.

It will be observed that, as predicted, the three points for the decay at 10, 20, and 30 seconds lie very well on a straight line for all the currents used. The measured data are not sufficient to determine whether the decay during the first 10 seconds is logarithmic with time.

If the overvoltage is due to active hydrogen which diffuses away from the interface into the body of the solution, then the rate of de-

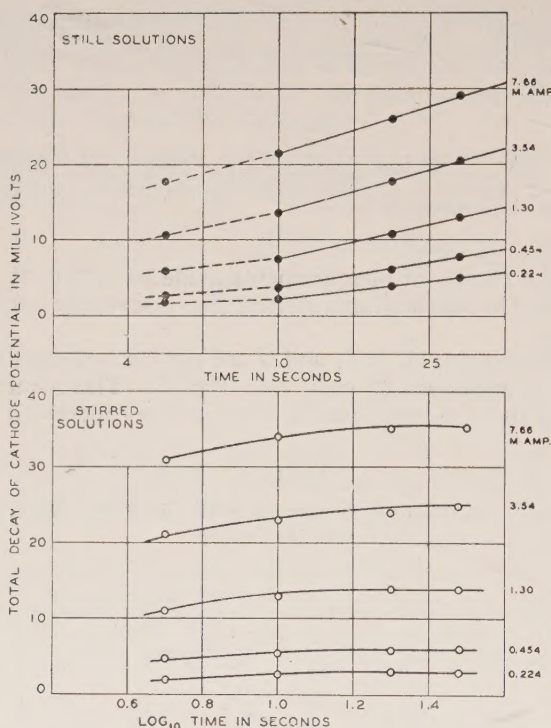


FIG. 5. Cathode overvoltage decay in hydrogen solutions.

cay of cathode potential after the polarizing circuit is opened should be much greater in a stirred solution. Also, the actual concentration at the interface for a given current density, and thus the overvoltage at that current density, should be less in a stirred solution. The next series of experiments was carried out to test this prediction.

Oscillograms were taken of the decay of cathode overvoltage in solutions *stirred* by a rapid stream of hydrogen which passed up directly in front of the electrode. The range of currents used to polarize the electrode was the same as that used in still solutions. Typical oscillo-

grams in stirred solutions are shown in the bottom line of Fig. 3 and the middle line of Fig. 4. In each case the polarizing current was interrupted at *c* and the cathode potential decayed in the positive direction along *cd*.

As in still solutions, none of the curves taken in stirred solutions showed an initial vertical drop. In all stirred solutions, however, the potential of the cathode decayed much more rapidly, as was predicted, and reached the reversible value within 20 to 30 seconds. Beyond point *d* in Fig. 3 and 4 the curve is horizontal and corresponds to the reversible hydrogen potential.⁵

Measurements taken from a series of curves similar to Fig. 3 and 4 for the same current densities as used with still solutions, and the stable cathode potential corresponding to each current are given in Table II. The data in columns 3, 5, 7, and 9 are plotted against the logarithm of time in the lower set of curves in Fig. 5. Here as in still solutions

TABLE II
Cathode Overvoltage Decay in Stirred Solutions Saturated with Hydrogen

Current in millamp.	Cathode Potential in millivolt	Total Decay of Overvoltage after							
		5 Sec.		10 Sec.		20 Sec.		30 Sec.	
		mv.	%	mv.	%	mv.	%	mv.	%
0.224	—3	2.0	67	2.7	90	3.0	100	3.0	100
0.454	—6	4.6	77	5.3	88	5.8	97	6.0	100
1.30	—14	11	79	13	93	14	100	14	100
3.54	—26	21	81	23	88	24	92	25	96
7.66	—37	31	84	34	92	35	95	35	95

the rate of decay during the first 5 seconds of decay increases with an increase in the current density used to polarize the cathode.

A comparison of the overvoltages in the second column of Tables I and II shows also, as predicted, that for the same current the overvoltage in the stirred solution is much less than in the still solution. It is to be observed that the difference is *much* greater at the lower currents and might even disappear at sufficiently high currents. This fits in nicely with the proposed theory since at low currents there is practically no stirring due to hydrogen evolution, but as the current is increased the stirring due to this cause increases and at sufficiently high currents might even mask the stirring effect due to bubbling hydrogen around the electrode.

Although the films could be measured with an accuracy of ± 0.1 millivolt, in the case of decay in *stirred* solutions it was impossible to assign an exact potential to the points *c* where the polarizing current

⁵ The expression "reversible hydrogen potential" is confined in this paper to the potential of a platinized platinum electrode in the same solution at a pressure of hydrogen gas corresponding to that over the solution under the prevailing atmospheric conditions of pressure and temperature. All other equilibrium potentials, even though they may be reversible, are designated as "stable potentials;" this distinction is used purely for purposes of convenience of distinction in the discussion.

was interrupted. This was due to the irregularities in the lines which correspond to the polarized potential on the several films. The potential corresponding to the start of the decay and recorded in column 2 was not taken from the curve but was the potentiometer reading and, of course, was a sort of average of the actual fluctuating values. If the actual value at the instant the circuit was opened did not correspond to the potentiometer reading, then all points measured would obviously be in error by an amount equal to the error in the potential assigned to the point *c*, which might amount to 3 millivolts for the two largest currents. This would easily account for the apparent lack of 100% decay to the reversible value after 30 seconds indicated in the last column.

The magnitude of the maximum vertical variations in the lines preceding the point *c* for the various currents used and the potentials which they represent are given in Table III. Though these fluctuations in potential are too small to be of significance, yet their persistence and unquestionable dependence upon current density cause them to deserve further consideration. That they are not caused by *IR* drop through

TABLE III
*Magnitude of the Maximum Vertical Variations in the Lines
Preceding the Point C*

Current in milliamp.	0.224	0.454	1.30	3.54	7.66
Variation in Vertical Position of Line in mm.	0.5	1.2	2.6	3.4	4.9
Corresponding Variation in milli- volts.	0.3	0.7	1.4	1.9	2.8

a variable resistance due to a gas film on the electrode or the rapid stream of gas bubbles used for stirring, is demonstrated by the fact that there is not the proper relation between current change and potential change; and a much more conclusive fact is that a fall of potential across a fluctuating resistance would cause, at the beginning of the decay curve, a vertical drop, the length of which would correspond to the product of the current times the instantaneous value of the resistance. On *no* oscillogram, however, did such a vertical drop appear. On all the oscillograms taken in stirred solutions, the beginning of decay had a definite and measurable slope. This is clearly seen in Fig. 3 and 4.

It is suggested that the fluctuations observed are due to very rapid changes in the effective concentration of hydrogen atoms and ions at the interface caused by rapid changes in the effective current density. These rapid changes in the current density might result from changes in the conductivity of the electrolyte at the interface and from changes in current density resulting from rapid fluctuations in the amount of electrode surface covered by gas.

All of these data for both still and stirred solutions saturated with hydrogen support the theory of polarization and overvoltage proposed in the introduction. The next series of experiments is similar to the

one just described except that the solutions are saturated with nitrogen. According to the theory, the stable cathode potential at a given current density should be less in these solutions than in the hydrogen-saturated solutions, and less in the stirred than in the still solution.

Solutions Saturated with Nitrogen. Fig. 6 is an oscillogram typical of those recording the decay of cathode potential in *still* solutions saturated with nitrogen. The point *a* in each curve represents the instant at which the polarizing current was interrupted. Here, as with hydrogen-saturated solutions, there was no initial vertical drop in the curve at any current used. The general form of the decay was the same for all currents, from 0.047 to 7.72 milliamp.

These curves and data provide unusually interesting and valuable information. One highly significant point is evident from the lowest current recorded; although here hydrogen is actually being liberated at a potential 6 millivolts *more positive* than the reversible hydrogen poten-

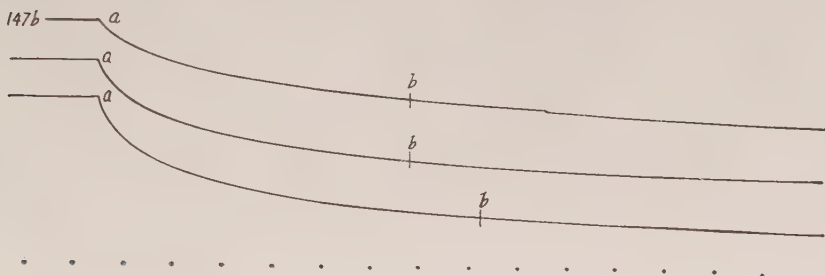


FIG. 6. Cathode overvoltage decay in still solutions saturated with nitrogen.

	Top Line	Middle Line	Bottom Line
Charged potential	-0.013 v.	-0.017 v.	-0.020 v.
Current density/cm. ²	0.457 milliamp.	0.910 milliamp.	1.33 milliamp.
Amplification system	1	1	1
Timing dots at 10 sec. intervals.			

tial, yet the nature of the decay curve is the *same* as of those which start from values *more negative* than the reversible value. An equally interesting fact is that all of the other curves, though starting from some negative or overvoltage value, decay *right through the reversible value without an inflection of any sort*. These curves furnish strong evidence in support of the view that the mechanism of the electrode process is essentially the same above, at and below the reversible value; or, in other words, that there is nothing unique about the mechanism at the so-called reversible electrode.

The reversible potential in the curves of Fig. 6 is indicated in each case by the line drawn through the curves at *b*. The positive potential at which the decay would eventually end was not determined.

In *still solutions saturated with nitrogen* the form of the decay was *not* dependent upon the length of time at which the cathode was held at the polarized potential.

This means that the active atomic hydrogen accumulates up to a definite concentration for each current and thus produces a definite overvoltage under a given set of conditions. The rate of removal

having become equal to the rate of formation, there is no continuous building up of a reserve in the electrode or solution as time goes on.

Fig. 7 shows decay curves following a charge at 0.459 milliamp. for varying periods of time. The top line represents the decay after 7

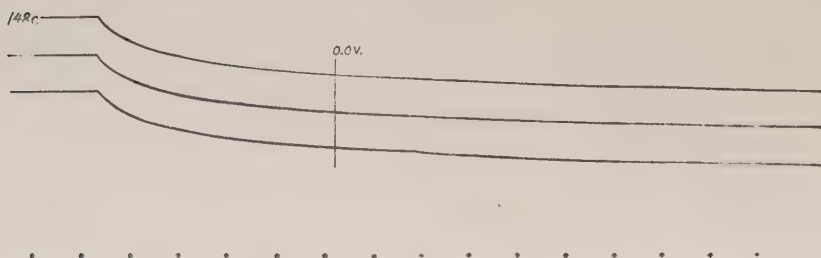


FIG. 7. Decay of cathode potential in still solutions saturated with nitrogen. Duration of charge was 7 min. for top line, 30 min. for middle line, and 60 min. for bottom line. In all cases the charged potential was -0.010 v., current density was 0.459 milliamp./cm.², amplification system 7, and timing dots at 10 sec. intervals.

minutes of charging; the middle line, after 30 minutes of charging; and the bottom line, after 60 minutes of charging. The stable polarized potential was -0.010 volt and did not change with time in any case. The line designated as 0.0 volt on the film corresponds to the reversible potential on all three lines. This lack of dependence of the manner of decay upon the duration of the preceding charge is manifest whether the polarized potential is more *positive* or more *negative* than the reversible value.

TABLE IV

Decay of Cathode Potential in Still Solutions Saturated with Nitrogen

Current in milliamp.	Cathode Potential in mv.	Total Decay in Millivolts after		
		5 Sec.	15 Sec.	30 Sec.
0.047	+6	0.6	1.5	2.0
0.103	-1	1.2	2.7	4.3
0.226	-6	2.1	4.5	6.7
0.457	-13	3.7	7.1	10.0
0.910	-17	5.9	10.6	13.7
1.33	-20	7.2	12.3	16.1
3.85	-28	14.7	20.8	25.2
7.72	-35	23.1	30.5	34.5

In Table IV are the stable cathode potentials corresponding to the respective currents, and also data obtained from measurements of a set of oscillograms showing the decay of potential in still solutions saturated with nitrogen. A comparison of the values for cathode potentials in this and in Table I shows that the stable values in the nitrogen solution for corresponding currents are much less than in the hydrogen solutions, as was predicted should be the case.

The decay potentials from Table IV are plotted against the logarithm of the corresponding time in the upper set of curves of Fig. 8. It will be observed that during the first 30 seconds of decay the process is strictly logarithmic with time, and that here, again, as expected, the rate of decay increases with an increase in the current used to polarize the cathode.

Comparison of the upper sets of curves in Fig. 5 and 8 shows that, whereas the rate of decay in still solutions of nitrogen is initially

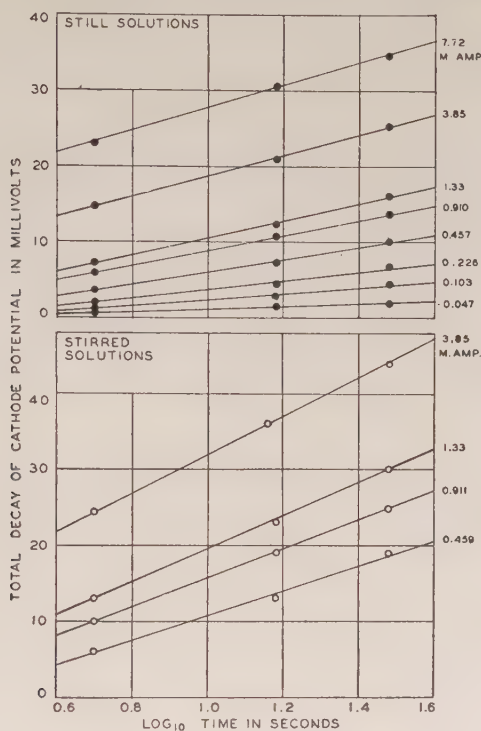


FIG. 8. Decay of cathode potential in nitrogen solutions.

greater than that in still solutions of hydrogen, as would be expected, however, the rates in the two cases become approximately the same after 10 seconds of decay following a charge at a given current density. The slopes of the V-log time curves in Fig. 5 between 10 and 30 seconds are the same as the slopes of the lines in Fig. 8 for the corresponding currents. These slopes for the various currents are given below in Table V. The equality of slopes under these conditions was not anticipated. A possible explanation is that in these still solutions the layer some distance away from the electrode in the nitrogen-saturated solution may have become fairly well saturated with hydrogen and thus not so much different from the hydrogen-saturated solution, since in all cases the current was passed through the solution at least

TABLE V

Slopes of V-Log Time Curves for Decay of Cathode Potential in Still Solutions

H ₂ Solutions		N ₂ Solutions	
Current in milliamp.	Slope $\times 10^3$	Current in milliamp.	Slope $\times 10^3$
0.224	6.0	0.226	6.0
0.454	8.5	0.457	8.1
1.30	11.6	1.33	11.4
3.54	13.9	3.85	13.4
7.66	15.6	7.72	14.6

fifteen minutes before the oscillograms were taken. Some support to this explanation is furnished by the results in a stirred solution saturated with nitrogen, recorded in Table VI. Under these conditions the decay is far more rapid than in any other case even after 30 seconds.

The fact that the slopes recorded in columns 2 and 4 of Table V have the same value is not in accord with the theory of decay developed by Armstrong and Butler.⁶ According to this theory the decay of hydrogen overvoltage should be logarithmic with time; also the instantaneous value of the rate of decay should depend upon the instantaneous value of the potential, since, according to their theory, the

TABLE VI

Decay of Cathode Potential in Solutions Stirred by Nitrogen

Current in milliamp.	Cathode Potential in mv.	Total Decay in Millivolts after			Slope of V Log Time Curve. $\times 10^3$
		5 Sec.	15 Sec.	30 Sec.	
0.459	+13	6	13	19	16.6
0.911	+3	10	19	25	19.2
1.33	-2	13	23	30	21.8
3.85	-17	24	36	44	25.7

process of decay consists in the transfer of electrons at a rate which is proportional to e^{av} . The V-log time curves presented here, however, and the data of Tables I and IV show that although the *value* of the cathode potential after 10 seconds of decay in still solutions saturated with hydrogen is *considerably more negative* than the corresponding value in a still solution saturated with nitrogen, the *rate of decay* at 10 seconds, and up to 30 seconds, is the same in both cases. Hence the rate of decay cannot depend upon the value of the potential, and it is doubtful if decay is produced by a process, such as the transfer of electrons, whose rate is determined by the value of the potential.

Oscillograms showing decay curves in solutions *stirred* by a rapid stream of nitrogen are similar in general appearance to those taken in *still* solutions of nitrogen. Fig. 9 and 10 are typical of oscillograms

⁶ G. Armstrong and J. A. V. Butler, Trans. Faraday Soc. 29, 1261-66 (1933).

obtained under these conditions. Here there are even more striking illustrations of the liberation of hydrogen at potentials distinctly *more positive* than the reversible value. In Fig. 9 both lines represent the decay from polarized potentials which were *more positive* than the reversible value. Their general appearance, however, is identical with that of the curves in Fig. 10, both of which represent decay from

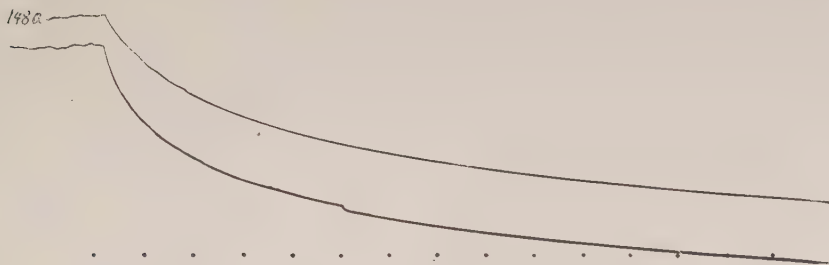


FIG. 9. Decay of cathode potential in solutions stirred by nitrogen. For the top line the charged potential was $+0.013$ v. and the current density 0.459 milliamp./cm.²; for the bottom line the charged potential was $+0.003$ v. and the current density 0.911 milliamp./cm.² For both curves the amplification system was 1 and the timing dots were at 10 sec. intervals.



FIG. 10. Decay of cathode potential in solutions stirred by nitrogen. For the top line the charged potential was -0.002 v. and the current density was 1.33 milliamp./cm.²; for the bottom line the charged potential was -0.018 v. and the current density 3.85 milliamp./cm.² For both lines the amplification system was 1 and the timing dots at 10 sec. intervals.

charged potentials *more negative* than the reversible value. The straight lines *b* in Fig. 10 are drawn at positions which correspond very nearly to the reversible potential. *These curves, as was observed with still solutions, show no inflection at all as the potentials decay through the reversible value.*

The fluctuations in the potential of the polarized cathode appear on Fig. 9 and 10 as on previous oscillograms showing the potential of a polarized cathode in stirred solutions. The fluctuations have approximately the same magnitude as those observed in solutions stirred by hydrogen and were probably due to the same cause. That they could not have been due to the fall of potential across a fluctuating resistance in this case is again shown on all oscillograms by the absence of any initial vertical drop.

In solutions stirred by nitrogen it was likewise true that the manner of decay following all currents was not dependent on the duration of the

current. Fig. 11 shows the decay, in solutions stirred by nitrogen, after a polarizing current of 3.85 milliamp. had been passing for 10 minutes, and after 30 minutes. The stable polarized potentials in both cases were equal and the decay curves run parallel throughout their extent.

Fig. 6, 9, and 10 were taken using the same amplification, and comparison of these curves reveals that the rate of decay in solutions stirred by nitrogen is considerably greater than the rate of decay in still solutions of nitrogen. This is confirmed by the data of Table VI which were obtained by measuring oscillograms showing decay in stirred solu-

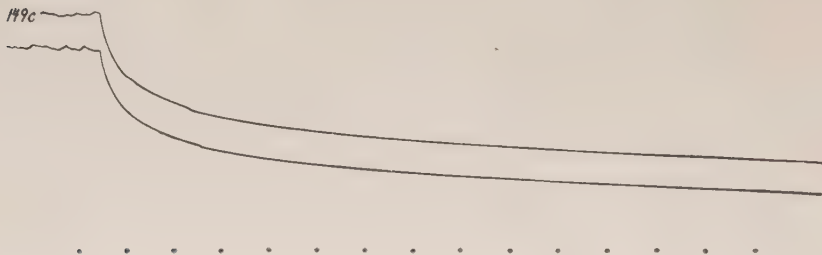


FIG. 11. Decay of cathode potential in solutions stirred by nitrogen. The top line represents the decay after 10 min. of charge, and the bottom after 30 min. of charge. In both cases the charged potential was -0.016 v., the current density 3.85 milliamp./cm.², the amplification system 3, and the timing dots at 10 sec. intervals.

tions. These data are plotted against the logarithm of time in the lower set of curves in Fig. 8. In this case, as in all previous cases, the rate of decay is some function of the current density used to polarize the cathode.

SUMMARY

The following observations have been made in this paper about the decay of polarized potentials at a platinized platinum cathode:

1. The rate of decay in all cases is independent of the duration of the preceding cathodic polarization.
2. The rate of decay in all cases increases with the current density used to polarize the cathode.
3. After about 10 seconds the rate of decay in still solutions saturated with nitrogen is the same as the rate in still solutions saturated with hydrogen, in spite of the fact that the value of the potential in the former case is considerably more positive than in the latter case.
4. In solutions saturated with nitrogen the decay curve passes right through the reversible value with no change in curvature whatsoever. In those cases where the stable, polarized potential is more positive than the reversible value, the general form of the decay curve is identical with that when the polarized potential is more negative than the reversible value.
5. In still solutions saturated with hydrogen the potential does not decay to the reversible value within several minutes; in solutions stirred

by hydrogen, however, the potential decays to the reversible value within 20 to 30 seconds.

6. In stirred solutions the rate of decay is greater than in still solutions, other conditions being the same.

7. The stable cathode potential for any current density is most negative in still solutions saturated with hydrogen and is progressively less in still solutions saturated with nitrogen, stirred solutions saturated with hydrogen, and stirred solutions saturated with nitrogen.

8. Hydrogen in the gaseous state has been formed at potentials more positive than the reversible values as that expression has been defined for use in this paper.⁷

These observations lend strong support to the conclusion that the rate-determining factor in the decay of any polarized potential on open circuit is the diffusion of hydrogen away from the electrode-solution interface. This conclusion involves the hypothesis suggested in an earlier paper² that the potential at an electrode is at all times determined by the activity of hydrogen ions and hydrogen atoms at the interface. If, as was true in this study, the activity of hydrogen ions is practically constant, any variations in potential would be due to changes in the activity of hydrogen atoms. It is considered that the results of this study support this hypothesis. They indicate, further, that the primary factor determining the hydrogen atom activity, and therefore the instantaneous value of the potential, is the rate of diffusion of hydrogen to, or away from, the interface.

ACKNOWLEDGMENT

The junior author wishes to acknowledge his indebtedness to the Julius Rosenwald Fund for fellowship grants which made this work possible.

Resumen del artículo: "Estudios de Sobrevoltaje. XIII. Desaparición del Potencial Catódico en Soluciones Saturadas con Hidrógeno o con Nitrógeno, Calmas y Agitadas"

La desaparición natural del sobrevoltaje de catodos de platino platinizados se estudia mediante oscilogramas. Los resultados indican que la razón de la desaparición (a) es independiente de la polarización catódica previa; (b) aumenta con la densidad de corriente usada para la polarización del cátodo; (c) es mayor en soluciones agitadas; (d) es la misma después de 10 segundos en soluciones calmas saturadas bien con H_2 o N_2 .

El potencial catódico estable para cualquier densidad de corriente es el mas negativo para soluciones calmas saturadas con H_2 ; es progresivamente menos negativo en solns. calmas sat. con N_2 , solns. agitadas saturadas con H_2 y solns. agitadas sat. con N_2 .

⁷ See footnote 5.

STUDIES ON OVERVOLTAGE. XIV.
A STUDY OF HYDROGEN DECOMPOSITION POTENTIALS UNDER
VARIOUS CONDITIONS IN ACID SOLUTIONS AT
PLATINIZED PLATINUM ELECTRODES*

By A. L. FERGUSON** AND MYRON B. TOWNS***

ABSTRACT

This paper is a study of the influence on cathode charge curves, for platinized platinum cathodes in 2 *N* H₂SO₄, of conditions that alter the hydrogen concentration on the solution side of the electrode-electrolyte interface. The purpose is to secure information relative to a theory of polarization potential proposed in a previous paper by the senior author. The results show definitely that the cathode potential, both below and above the so-called reversible value, can be materially altered for a given current density by conditions on the solution side of the interface which influence the rate of diffusion of hydrogen away from or to the interface. The changes produced are all such as were expected on the basis of the proposed theory.

INTRODUCTION

The preceding paper in this series¹ described and discussed experiments in which a platinized platinum electrode was allowed to decay on open circuit after it had been cathodically polarized at different current densities under the four conditions: (1) a still solution saturated with hydrogen; (2) a stirred solution saturated with hydrogen; (3) a still solution saturated with nitrogen; and (4) a stirred solution saturated with nitrogen.

The decay curves in all cases were logarithmic with time; however, the rate of decay and the final potential values reached were different for the different conditions. The rate of decay was least in still solutions saturated with hydrogen and greatest in stirred solutions saturated with nitrogen.

In all solutions saturated with nitrogen, the potential decayed right through the so-called reversible value, giving no indication whatsoever

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¹ See page 307 this volume.

of such a value. This fact was interpreted as indicating that there is nothing unique about the nature of the processes which occur at the reversible potential as compared to the processes taking place at potentials above or below this value.

Under all conditions otherwise the same, the rate of decay increased with increase in current density used to produce the original polarization.

For the same current density the stable value of cathode polarization was different for the respective conditions, being most negative in still solutions saturated with hydrogen and least negative in stirred solutions saturated with nitrogen.

These results point to the rate of diffusion of hydrogen away from the electrode surface as a primary factor determining cathode polarization and its rate of decay. All of which lend material support to the theory proposed previously² to the effect that the potential of a platinized platinum electrode below, at, or above the so-called reversible[†] value is determined by the activity of hydrogen atoms and ions at the interface.

In the previous paper, no special attention was paid to the charging process; interest was confined to the discharge curves obtained from different polarized cathode values. The results indicated that a detailed study of charge curves obtained under similar conditions should provide some interesting information.

In the present paper, current-potential data have been obtained with platinized platinum electrodes in 2 *N* sulfuric acid in still and stirred solutions, saturated in one case with hydrogen and in another with nitrogen. The cell and apparatus used in these experiments are the same as those described in Part XIII.¹ As before, all potentials are given with respect to the potential of a platinized platinum electrode in 2 *N* sulfuric acid saturated with hydrogen at 25° C. as zero

EXPERIMENTAL

Solutions Saturated with Hydrogen. In still solutions saturated with hydrogen the *currents* were *constant* and covered the range between 2×10^{-6} and 1.3×10^{-2} ampere. The overvoltages observed are recorded in the third column of Table I. Three different cathodes were used in obtaining these data, and the potentials observed for a given current at different times did not vary by more than 2 millivolts. Those recorded are the means of the several values observed with all three electrodes; the uncertainty in each value recorded is ± 0.001 volt.

To achieve this reproducibility, however, it was necessary to use a fresh electrode. The cathode potential for a given current was more negative than the value in column 3 of Table I with an electrode that had been used at higher currents where there was vigorous evolution of hydrogen gas; about 0.1 milliamp. seemed to be the upper limit of the current that could be used and still maintain reproducibility.

² A. L. Ferguson and H. Bandes, *Trans. Electrochem. Soc.* **81**, 291 (1942).

[†] The expression "reversible hydrogen potential" is confined in this paper to the potential of a platinized platinum electrode in the same solution at a pressure of hydrogen gas corresponding to that over the solution under the prevailing atmospheric conditions of pressure and temperature. All other equilibrium potentials, even though they may be reversible, are designated as "stable potentials;" this distinction is used purely for purposes of convenience of distinction in the discussion.

Similar lack of reproducible potentials resulted when an electrode was used which had stood idle in a solution saturated with hydrogen. This phenomenon is very similar to observations reported by others.³

TABLE I
Current-Potential Data for Platinized Platinum Electrodes
in 2 N Sulfuric Acid

Current in Milliamp.	Log ₁₀ Current in Amp. x 10 ⁶	Stable Polarized Cathode Potential in Volts			
		Hydrogen Solutions		Nitrogen Solutions	
		Still	Stirred	Still	Stirred
0.0020	0.30	0.000	0.000	+0.088	+0.092
0.0054	0.73	0.000	0.000	+0.038	+0.072
0.0096	0.98	-0.001	0.000	+0.022	+0.061
0.0196	1.29	-0.002	0.000	+0.015	+0.051
0.0468	1.67	-0.005	0.000	+0.006	+0.040
0.103	2.01	-0.007	-0.001	0.000	+0.030
0.132	2.12	-0.008		-0.001	
0.224	2.35	-0.010	-0.003	-0.005	+0.021
0.452	2.66	-0.014	-0.005	-0.010	+0.012
0.895	2.95	-0.017	-0.009	-0.014	+0.004
0.911	2.96			-0.016	+0.003
1.30	3.11	-0.019	-0.012	-0.017	-0.001
3.85	3.59	-0.028	-0.022	-0.027	-0.016
7.73	3.89	-0.035	-0.030	-0.034	-0.026
9.25	3.97			-0.037	-0.030
13.5	4.13	-0.043	-0.039	-0.042	-0.037
17.5	4.24			-0.047	-0.042

It seems to indicate that the ability of the electrode to promote the rate-determining cathode reaction, whatever it may be, is lessened by the continued presence of hydrogen on the electrode surface. Such a "de-activated" electrode could be restored to the condition of a fresh electrode by making it the anode until oxygen was evolved, followed by sufficient cathodic polarization to bring the potential back to, or at least only slightly more positive than, the reversible hydrogen potential.

Fig. 1 (upper line) shows the cathode potentials of column 3 of Table I for *still* solutions plotted against the logarithm of the current. The overvoltage at the two smallest is recorded as zero because they amounted to only a few tenths of a millivolt, whereas results here are expressed to the nearest millivolt. There was, however, in *still* solutions, a measurable overvoltage even at the *smallest* current density. This observation does not coincide with those of Bowden⁴ and Wirtz⁵ who report no overvoltage at all on platinized platinum at currents less than 1×10^{-4} amp./cm.²

It might be well to emphasize that all of the polarized cathode potentials in Table I are those representing a steady state at the electrode;

³ H. T. Beans and L. P. Hammett, J. Am. Chem. Soc. **47**, 1215 (1925); F. P. Bowden, Proc. Roy. Soc. **126A**, 107 (1929); S. Popoff, A. H. Kunz and R. D. Snow, J. Phys. Chem. **32**, 1059 (1928); M. Volmer and H. Wick, Z. physik. Chem. **172A**, 429 (1935).

⁴ F. P. Bowden and E. K. Rideal, Proc. Roy. Soc. **120A**, 59 (1928).

⁵ K. Wirtz, Z. physik. Chem. **36B**, 435 (1937).

that is, these potentials showed no tendency to change with time over a period of 15 minutes after the potential became constant. It should be noted especially that, whereas the range of currents here is the same as that used by Bowden,⁴ the upper curve in Fig. 1 is *not at all linear* as found by Bowden for platinized platinum. It is upon a *linear* relation that Bowden bases some of his most important calculations and conclusions.

The current-potential data in solutions *stirred* by a rapid stream of hydrogen passing up directly in front of the electrode were also obtained using *constant currents*. The observed potentials are given in the fourth column of Table I, and the volt-log i curve is shown in the bottom line of Fig. 1. In this case two different electrodes were used and the values obtained at different times with each did not vary by

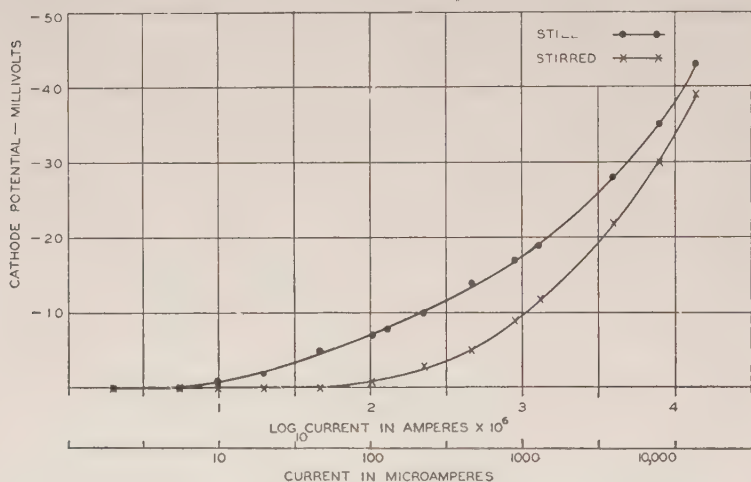


FIG. 1. Cathode potential-log current curves for platinized platinum cathodes in 2 *N* sulfuric acid saturated with hydrogen.

more than 2 millivolts. The uncertainty in each value is ± 0.001 volt, but to obtain this reproducibility it was again necessary to use a fresh electrode or one that had been "activated" by the means described above. In stirred as well as in still solutions the prolonged presence of hydrogen produced a "de-activated" electrode, this inactivity being made manifest, as before, by more negative polarized potentials for a given current.

The cathode potentials in stirred solutions likewise correspond to a steady state at the electrode; they were absolutely stable, after becoming constant, over a period of 15 minutes. For these stirred solutions, also, the cathode potential-log current curve is *non-linear* throughout its extent. Hickling and Salt⁶ report a *linear* volt-log i curve for platinized platinum with a slope of 0.02. The current densities used by them, however, were much larger than those used here

⁶ A. Hickling and F. W. Salt, Trans. Faraday Soc. **36**, 364 (1940).

and extend from 0.001 to 1.0 amp./cm.² The straight lines joining the last two points in the curves of Fig. 1 have slopes of 0.033 for the still solution and 0.038 for the stirred solutions.

At currents slightly less than 0.5 milliamp. in still solutions, hydrogen collected in small bubbles around the edges of the electrode; but at currents larger than 0.5 milliamp. small bubbles appeared at several points on the electrode surface and escaped from these points. It is interesting, and perhaps significant, that the maximum difference between the potentials in still and stirred solutions occurred at this particular current of about 0.5 milliamp. The indications are that this difference would disappear at currents slightly larger than those used in this study. In *stirred* solutions no measurable overvoltage appeared for currents less than about 50 microamp. Throughout the range of currents used here, the cathode potential in stirred solutions was more positive than that in still solutions for the same current. These facts make it appear that the difference between polarized cathode potentials in still and in stirred solutions is due to a *concentration polarization* of some nature that exists in *still* solutions.

Solutions Containing No Hydrogen. Current-potential data in solutions saturated with pure nitrogen reveal the behavior of a polarized cathode when all electromotively active gases are initially absent, and when the only hydrogen present is that liberated by electrolysis. Two methods of polarizing the cathode were used: in one case the current was supplied from a *constant potential* obtained by putting a potential divider across a 12-volt storage battery; in the other case, a *constant current* was supplied by two heavy-duty 45-volt dry cells in series with a high resistance.

In polarizing the cell by the constant potential method, the potential of the cathode depended upon the length of time that elapsed between application of the potential and its measurement. When the polarizing circuit was first closed, the current through the test electrode rose immediately to a peak value and then diminished with time. This phenomenon was shown on oscillograms of Ferguson and Bandes⁷ and is satisfactorily explained by them as due to the discharge of hydrogen ions to hydrogen atoms which caused the cathode to develop an opposing negative potential. In order that measurements might be comparable, the cathode potential and current were measured in all cases 15 minutes after closing the polarizing circuit. It was also important that all polarization occur at the cathode, because any change in the potential of the anode would of necessity influence the cathode potential since the total polarizing potential was constant. To make certain that such was the case, a polished copper rod was used as the anode, and to prevent any concentration polarization the electrolyte was allowed to drain past the copper rod while the solution in the anode chamber was stirred by a stream of nitrogen. The potential of this anode did not vary more than 0.4 millivolt during any one series of measurements.

Measurements made by this method in *still* solutions are given in the first two columns of Table II and these data are plotted with the solid

⁷ A. L. Ferguson and H. Bandes, Trans. Electrochem. Soc. **81**, 273 (1942).

circles in Fig. 2. This curve is the familiar decomposition potential curve, and for convenience the initial, nearly horizontal part will hereafter be called the positive branch, and the nearly vertical part will be called the negative branch of the curve. The cathode potentials observed on the positive branch reached their stable, polarized potentials very slowly. This ceased to be true for currents larger than about 50 microamp. where the potential, however, was still *more positive* than the reversible hydrogen value. From this point on to larger currents, a stable cathode potential was reached rather quickly and it did not

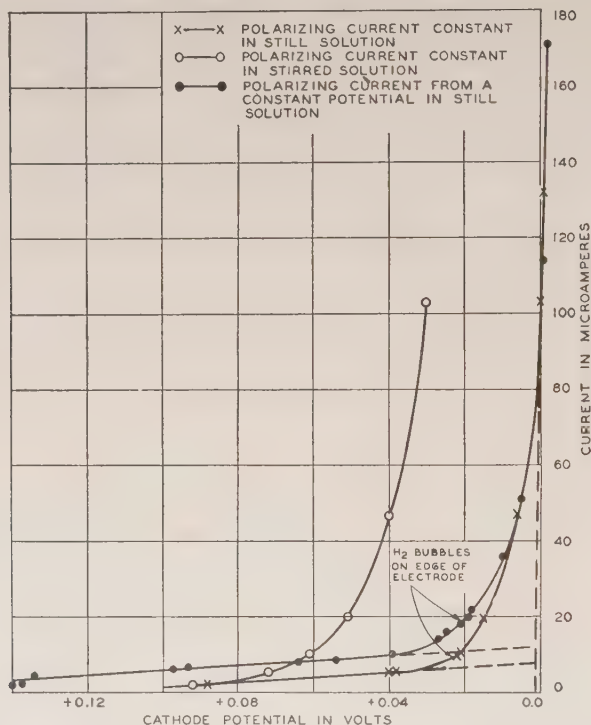


FIG. 2. Current-potential curves for platinized platinum in 2 *N* sulfuric acid saturated with nitrogen.

change with time over a period as long as 60 minutes. *It is most interesting to note that small bubbles of hydrogen could be seen adhering to the edges of the electrode when the cathode potential was +0.02 volt, which corresponded to a current of about 20 microamp.* That these bubbles were not dissolved nitrogen separating out on the edges was proved by the fact that no bubbles appeared if the electrode was allowed to stand on open circuit. Evolution of hydrogen as bubbles at various spots on the electrode surface did not begin until there was an overvoltage of about 2 millivolts, corresponding to a current of about 0.2 milliamper.

TABLE II

Current-Potential Data for Platinized Platinum Electrodes in Still Solutions of 2 N Sulfuric Acid Saturated with Nitrogen

Current from a Constant Potential in Microamp.	Stable Polarized Cathode Potential in Millivolts*	Constant Current from High Potential in Microamp.	Stable Polarized Cathode Potential in Millivolts
2.3	+140	2.0	+88
2.4	+137		
4.7	+134	4.9	+40
6.2	+97	5.4	+38
6.6	+93		
7.8	+64		
8.4	+54	9.6	+22
10.1	+39	10.1	+21
13.8	+27		
16.0	+25		
17.8	+21		
19.9	+19	19.6	+15
22.3	+18		
36.2	+10		
51.3	+5	46.8	+6
114.	-1	103.	0.0
		132.	-1
171.	-2		

* These are potentials measured 15 minutes after closing the polarizing circuit.

On the positive branch of the decomposition potential curve the only test of reproducibility was to see whether points measured at different times fell on the same smooth curve. Those recorded in column 2 of Table II are taken from three different series of measurements; all three series, however, were measurements with the same electrode. For this one electrode the reproducibility is quite satisfactory. Measurements using a *constant potential* as the source of polarizing current were not carried out with currents higher than those shown in Table II.

Columns 3 and 4 of Table II give the results of using a *constant current* as the polarizing device in *still* solutions saturated with *nitrogen*. These data are plotted with the crosses in Fig. 2. The potentials on the positive branch of the decomposition potential curve were more negative for a given current than the corresponding values obtained by using a constant polarizing potential. It is reasonable to suppose that the cathode potentials observed on the positive branch with a constant current are the limits which would be approached after a very long time by the potentials for the same current using a constant polarizing potential. For very small constant currents (2 to 10 microamp.) several hours passed before the cathode potential became constant. After becoming so, however, the stable polarized values showed no tendency to change with time, and were constant over periods of 60 minutes. Further, the polarized cathode potentials using a constant current were reproducible to ± 0.001 volt with fresh, or "active,"

electrodes. Those recorded in the fourth column of Table II are the means of measurements made with seven different electrodes at different times.

In still solutions saturated with nitrogen, characteristics of an inactive electrode did not appear if the electrode simply stood on open circuit. Further, when used as a cathode during electrolysis, reproducible current-potential data could be obtained provided the currents used did not exceed a value of about 1×10^{-4} amp. If larger currents than this were used, the stable, cathodically polarized potentials for a given current were found to become more negative with each successive determination. A current of 4.5×10^{-4} amp., for instance, used in still nitrogen solutions over a period of several days gave the following cathodically polarized potentials on successive days: -0.010 , -0.011 , -0.016 , -0.017 , and -0.019 volt.

As pointed out above for *constant potential* polarization, gas bubbles were evident on the edges of the electrode at a *positive* potential of 0.02 volt, corresponding to a current of 2×10^{-5} amp. For *constant current* polarization small bubbles of hydrogen again appeared around the edges of the electrode at a potential of about $+0.02$ volt. The current passing in this case, however, was about 1×10^{-5} amp.

Current potential measurements using a *constant current* in *still* solutions saturated with *nitrogen* were obtained through the whole range of currents from 2×10^{-6} amp. to 17×10^{-3} amp. The complete set of current-potential data obtained in this way is given in the fifth column of Table I. The first seven items in this table, of course, are identical with the corresponding items in the last two columns of Table II. The data in Column 5 of Table I are reproducible to ± 0.001 volt and are the means of measurements made with six different fresh, or "active," electrodes.

The volt-log i curve for these values is shown in the upper curve of Fig. 3. This curve has two linear portions. The linearity of the middle portion begins at a current of about 5×10^{-5} amp. and ends at a current of about 5×10^{-3} amp. where the cathode potentials are, respectively, $+0.006$ volt and -0.030 volt. The slope of this portion is 0.016. The current and potential at which the linearity of this portion begins are the same as the current and potential at which the two decomposition potential curves of Fig. 2 become identical. The second linear portion of the upper curve in Fig. 3 has a slope of 0.037.

It is interesting to note that throughout the entire range of currents the cathode potentials in *still* solutions saturated with *nitrogen* were more *positive* than those in *still* solutions saturated with *hydrogen* (Table I). It appears, however, that this difference would disappear at currents larger than those used in this study. A reasonable explanation for the difference in this case is that in nitrogen solutions the pressure of hydrogen at the electrode surface was much less than one atmosphere at small currents due to diffusion of the molecules out into the body of the solution where their concentration was initially zero. At high currents the formation of hydrogen molecules exceeded the diffusion rate, and the pressure at the electrode surface, therefore, would be the same in the two solutions. Since both solutions were

still, any concentration gradient of hydrogen ions would be the same in both solutions for the same currents.

The last column of Table I gives the cathode potentials observed using constant currents in solutions stirred by a rapid stream of nitrogen passing up in front of the electrode. The values recorded here are averages of values taken with five electrodes at different times and were reproducible to ± 0.001 volt, with fresh, or "active," electrodes. In this case, also, the stable polarized potentials did not change with time over a period of 60 minutes. Part of these data are plotted with the open circles in Fig. 2, and the volt-log i curve for the complete range of currents is shown by the lower curve of Fig. 3.

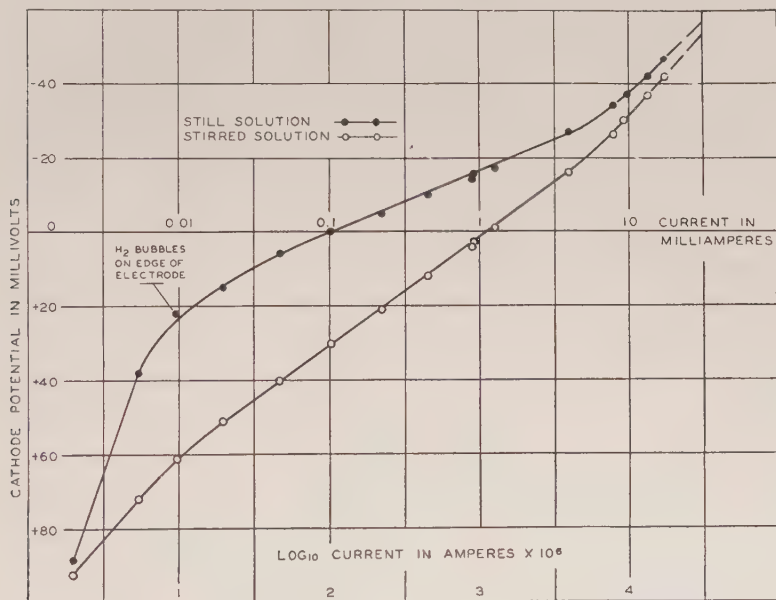


FIG. 3. Cathode potential-log current curves for platinized platinum in 2 N sulfuric acid saturated with nitrogen.

A highly noteworthy feature of both curves in Fig. 3 is that *each of them passes through the reversible hydrogen potential with absolutely no change in slope.*

The current-potential curve of Fig. 2 for solutions stirred with nitrogen shows in a striking manner the very *positive* cathode potentials at which hydrogen is liberated under these conditions; from Fig. 3 it may be seen that a current of 0.001 amp. is required to produce a polarized potential equal to the reversible hydrogen value. It must be true, however, that hydrogen is liberated at much smaller currents because in still solutions saturated with nitrogen small bubbles of hydrogen were formed by a current of about 1×10^{-5} amp. at a potential of +0.02 volt. If a current of 1×10^{-5} amp. evolves hydrogen in still solutions saturated with nitrogen, then the same current should

evolve hydrogen in solutions stirred by nitrogen. *This demonstrates beyond any question that hydrogen ions may be discharged at a potential at least as positive as +0.05 volt.* The more positive polarized potentials in stirred solutions for small currents must be caused by the low activity of atomic hydrogen. This is most likely due to rapid diffusion of atomic or molecular hydrogen into the body of the solution where the rapid stream of nitrogen tends to keep the concentration of molecular hydrogen at zero. At higher currents the rate of formation of atomic and thus molecular hydrogen increases to the point where it exceeds the rate of diffusion into the body of the solution. It can be seen from Fig. 1 and 3 that for currents of around 20 milliamp. and larger the cathode potential probably would become the same in both still and stirred solutions and independent of the nature of the saturating gas. A current of 50 milliamp., for instance, would probably produce an overvoltage of about 50 millivolts in all cases. In all solutions the slopes of the volt-log i curves approach each other at the upper end of the curves. The slopes are as follows:

Solutions saturated with hydrogen: still, 0.033; stirred, 0.038.

Solutions saturated with nitrogen: still, 0.037; stirred, 0.046.

DISCUSSION

Most of the recent theories of reversible and irreversible hydrogen electrodes⁸ have in common the assumptions that the transition from a hydrogen ion, or $H^+ (H_2O)_x$, to a hydrogen atom is a process requiring an energy of activation and that this process, therefore, is rate-determining during electrolysis when hydrogen is being evolved at the cathode. These assumptions lead directly to the result that

$$i = ae^{-bV} \quad (1)$$

where i is the current through the electrode, V is the stable, polarized potential, and a and b are constants at a particular electrode and temperature. The overvoltage exhibited when hydrogen is evolved during electrolysis is commonly called "activation overvoltage" by adherents of these theories. With the further assumption that the ions and electrons obey Boltzman statistics at the usual temperatures, the con-

stant b is found by all theories to have a value of $\frac{\alpha F}{RT}$ in which α is

put equal to 0.5 for reasons which differ in the various theories. The numerical value of $\frac{RT}{\alpha F}$ at 25° C. is 0.118 which agrees well with

slopes of volt-log i curves that have been observed by several investigators by whom metal electrodes other than platinized platinum were used.

⁸ F. P. Bowden, Proc. Roy. Soc. **126A**, 107 (1929); J. A. V. Butler, Proc. Roy. Soc. **157A**, 423 (1936); T. Erdey-Gruz and M. Volmer, Z. physik. Chem. **150A**, 203 (1930); H. Eyring, S. Glasstone, and K. J. Laidler, J. Chem. Phys. **7**, 1053 (1939); A. Frumkin, Acta Physicochim. **7**, 475 (1937); R. W. Gurney, Proc. Roy. Soc. **134A**, 137 (1931).

The much older Tafel theory differs from the newer theories mainly in the assumption that the rate-determining process during electrolysis is not the electrical discharge of ions but the combination of atoms into molecules. By making the additional assumptions that this combination of atoms is a second-order reaction and that the activity of hydrogen ions at the interface during electrolysis is the same as their activity on open circuit, one may arrive at an equation similar to (1)

$$\frac{RT}{2F}$$

in which b , however, has a value of $\frac{RT}{2F}$, or 0.029 at 25° C. The

numerical value of b in all of the theories is entirely the result of the additional assumptions made in an effort to describe the process mathematically. The numerical value of b depends upon certain assumptions which differ in the different theories.

The results obtained in the present study are not completely consistent with either of these theoretical approaches. The current-potential data show clearly that the stable polarized potential obtained with a given current is strongly influenced in some manner by conditions existing on the *solution* side of the double layer. They were more positive in solutions saturated with nitrogen than in solutions saturated with hydrogen at the same current; they were also more positive in stirred solutions than in still solutions. If, as the "activation" theories postulate, the rate-determining factor in the electrode reaction is the electrical discharge of ions, it must be explained how the rate of this process at a constant current is affected by stirring the solution or by changing the nature of the saturating gas. Such an explanation is not apparent.

Further, the "activation theories" demand that in solutions saturated with hydrogen the potential must be displaced *before* the current can flow. The theories also require that during the initial stage there must be a *linear* change of potential with time from the instant the charging circuit is closed. In the present study, however, it was found that, starting with an electrode at its equilibrium value in a solution saturated with hydrogen, considerable current, either anodic or cathodic, could flow with *no* displacement of the potential and, when the potential was changed, in neither case did it change linearly with time at the beginning.² Finally, each of the theories of "activation overvoltage" likewise predicts that the polarized potential is a linear function of the logarithm of the current density with a slope of 0.12. Under none of the conditions tried in the present work was this relation found to be true. In the case of stirred solutions of nitrogen the volt-log i curve was linear over a considerable range of current density, but the slope, 0.029, is one-fourth of that required by the theories just mentioned. It is, however, the slope obtained according to the Tafel theory. These facts point to the conclusion that on platinized platinum electrodes the rate-determining process is not the electrical discharge of ions by any mechanism at all.

The data gathered here appear to show conclusively that the equilibrium, reversible hydrogen potential cannot be regarded as the positive limit above which hydrogen ions may not be electrically discharged,

as the theories of Gurney,⁸ Erdey-Gruz and Volmer,⁸ Bowden,⁸ and of Eyring, Glasstone and Laidler⁸ require. The smallest constant current used in this study in solutions saturated with nitrogen resulted in a stable polarized potential that was considerably *more positive* than the reversible value. In absence of definite proof to the contrary, it is reasonable to conclude that electrolysis was proceeding at that potential with the discharge of hydrogen ions. The fact that bubbles of hydrogen were actually observed on the electrode at potentials appreciably more positive than the normal potential of a hydrogen electrode in the same solution is positive evidence that hydrogen can be produced at such positive values. The hydrogen bubbles are not due to any rise in temperature of the solution. It is shown in Table I that, even at a current as high as 1 milliamp. in solutions stirred by nitrogen, the electrode potential was still positive. Arguing further against the interpretation of the reversible hydrogen potential as the lowest negative (or most positive) potential for the discharge of hydrogen ions is the fact that, as the potential was made to pass through this value from more positive to more negative values, no change was observed at the reversible potential in the rate at which potential changed with time. This indicates that no new process begins, or that there is nothing unique in the electrode process taking place at the so-called reversible value. Further, the cathodic charge curves in hydrogen solutions contained no initial linear change of potential with time* that would be required if a potential-determining process were taking place (*e.g.*, changing the charge on a double layer, as assumed in the theories mentioned above) which process was proportional in extent to the quantity of electricity passed.

It was suggested in an earlier paper⁹ that the potential of the cathode is at all times due to two factors: (1) the activity of the hydrogen ions at the electrode-solution interface, which probably remained constant under all conditions of this research; and (2) the activity of atomic hydrogen at this same interface. According to this theory polarized potentials *more positive or more negative* than the reversible value involve either a deficiency or an excess of atomic hydrogen at the interface relative to that present at equilibrium under one atmosphere pressure. The rate-determining factor, therefore, during electrolysis becomes the process or processes by which atomic hydrogen is removed from the interface. Atomic hydrogen may be removed from the interface in several ways: (1) by re-ionization to form hydrogen ions; (2) by diffusion into the electrode as hydrogen atoms or molecules; or (3) by combination to form hydrogen molecules which may diffuse into the solution or combine to form bubbles. Conditions on the *solution* side of the interface alter the potential because these conditions greatly influence directly the rates of processes (2) and (3) and thus indirectly the rate of (1), and finally the stable polarized potential below, at and above the so-called equilibrium value.

The point of view is in qualitative agreement with the results of this study. The rate at which atomic hydrogen combines to form

* Note: This statement is based upon data at hand which will be published later.

⁹ A. L. Ferguson and H. Bandes, Trans. Electrochem. Soc. **81**, 291 (1942).

molecular hydrogen would be influenced appreciably by the rate at which molecular hydrogen is removed from the interface, and this would be greatly influenced by the concentration gradient existing between the interface and the body of the solution, regardless of whether the removal was achieved by bubble formation or by simple diffusion. For a given current, therefore, the polarized potential, or overvoltage, would be most negative in that solution where the concentration gradient of molecular hydrogen was lowest and the rate of escape least. In solutions previously saturated with hydrogen this condition would prevail in still solutions where the concentration gradient probably extends a considerable distance into the solution. In solutions stirred by hydrogen the concentration of molecular hydrogen a short distance from the electrode would be constant at that value characterizing a solution saturated under a pressure of one atmosphere, and the rate of diffusion away from the interface would be more rapid than in still solutions at the same current; the result should be a more positive potential, as was found (Table I).

If it is assumed that the overvoltage potential may be expressed as

$$V = \frac{RT}{2F} \log A_H + \text{const.} \quad (2)$$

where A_H is the concentration of atomic hydrogen at the interface, then values of A_H are obtained which are not unreasonable. A mathematical relation between current and potential is difficult to obtain with this hypothesis because expressions are not known which will give all the conditions affecting the rate of escape of atomic hydrogen as a function of the current density. It is only known that at a stable polarized potential

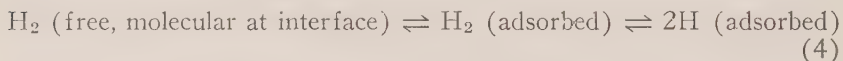
$$\frac{i}{2F} = - \frac{da_H}{dt} \quad (3)$$

Additional confirmation is obtained from the results in still solutions of nitrogen. In such solutions, at currents giving a potential in the overvoltage region, the concentration gradient of molecular hydrogen when a steady state has been reached would be very nearly the same as that in still solutions of hydrogen. The main difference would be that in nitrogen solutions the gradient would extend to a value of zero at some distance from the interface. The polarized potential, therefore, should be only slightly less negative than in still solutions saturated with hydrogen at the same current. That this is the case may be seen from an inspection of Table I where it may be observed that the cathode potentials in hydrogen solution are consistently a little more negative than in nitrogen solution at the same currents. Then again, in stirred solutions of nitrogen the concentration of molecular hydrogen would be zero beyond the diffusion layer and the potential in this case should be much more positive for a given current density due to the very rapid rate of escape of molecular hydrogen from the interface. That this is the case is evident from the last column of Table I where the

cathode potentials are considerably less negative than those in still solutions of both hydrogen and nitrogen at the same current densities.

At very large currents the rate of formation of molecular hydrogen would be so rapid, and the stirring action of the evolved bubbles so vigorous, that the concentration gradient in all types of solution would be identical. For such currents the polarized potential, according to the concentration theory proposed here, would no longer depend upon conditions in the body of the solution. The data in Table I indicate that at currents slightly larger than those used in this study the same potential would be observed in all cases.

Let us look more closely at the information given by solutions not previously saturated with hydrogen. In nitrogen-saturated solutions the initial concentration of molecular hydrogen is zero, and small currents result in polarized potentials more positive than the reversible value. If it is assumed that molecular hydrogen is formed in some way from adsorbed hydrogen, then at potentials much more positive than the reversible value probably the surface would be empty. At a constant applied potential in the positive region the current would equal the rate of escape of hydrogen atoms since any change in amount of adsorbed hydrogen atoms would alter the potential and this is arbitrarily held constant. However, one must consider also the equilibrium



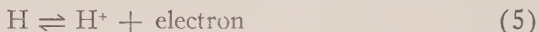
which means that the concentration of molecular hydrogen at the interface would probably vary in a linear way with the extent of the surface covered by adsorbed atoms. If, now, the potential is permitted to become more negative by increasing the applied potential, this means a greater extent of coverage of the electrode surface by hydrogen atoms, which results in a greater current and a greater concentration of molecular hydrogen. Hence, at very small currents the potential would change in a linear manner with the current.

As the applied potential is increased to more and more negative values, the currents become correspondingly larger since the rate of escape of molecular hydrogen from the surface becomes greater as the amount of coverage of the surface by hydrogen atoms is increased. Any particular current, of course, is that required to maintain such a concentration of hydrogen atoms at the interface as is necessary to produce a back potential equal to the applied potential. When the applied potential has become equal to the reversible value, the surface has become covered to such an extent that the molecular hydrogen at the interface is in equilibrium with the hydrogen gas in the solution and above the solution corresponding to one atmosphere pressure. From this point on, as higher potentials are applied, it is much more difficult to build up a higher concentration of hydrogen atoms on the electrode since they combine almost as rapidly as they are formed to give hydrogen molecules that escape. This results in a change in the current-potential relation, with the current increasing much more rapidly. It is possible, however, to build up temporarily higher concentrations of atomic hydrogen at the interface, or beneath the interface, to give po-

tentials more negative than the reversible value; *i.e.*, to give overvoltage.

The explanation of the decomposition potential curve (Fig. 2) given above is equivalent to the hypothesis that on the positive branch of the curve the rate of escape of molecular hydrogen is determined by the kinetics of the equilibrium shown in Eq. (4), whereas on the negative branch the rate of escape is governed to a large extent by the magnitude and extent of the concentration gradient of molecular hydrogen. At any potential on the negative branch of the curve there is a concentration of atomic hydrogen at the interface above the normal equilibrium value and this, in turn, generates a more negative potential. As can be seen from Fig. 2, the transition from one controlling process to the other is a gradual change, because the current-potential curve begins to change slope at a potential several millivolts more positive than the reversible value. At the current where the polarized potential equals the reversible value, the slope of the curve is that of the parts in the negative region of overvoltage potentials.

The evidence presented here can be explained by, and strongly supports, the theory that the potential of a hydrogen electrode is at all times determined by the effective concentration of hydrogen ions and hydrogen atoms at the interface. The potential is determined by the reaction



which is in stable equilibrium at all times. At potentials more positive than the so-called reversible value, the effective concentration of hydrogen atoms is proportional to the amount of electrode surface that is covered, and this is determined by the rate at which atoms combine to form molecules, or by the reverse process. One of the major factors involved here is the rate at which hydrogen molecules may be moved into or away from the interface. At potentials more negative than the reversible value the potential is still due to the effective concentration of atomic hydrogen at the interface, but much higher currents are needed to produce these higher concentrations due to the rapid escape of atomic hydrogen as molecular hydrogen. Here, also, a major factor is the rate at which molecular hydrogen may be moved away from the interface, and this is determined to a large degree by the concentration of hydrogen molecules in the body of the solution.

The data of this research also point to the conclusion that the equilibrium reversible potential exhibited by a platinized platinum electrode in a solution of a certain hydrogen ion activity differs from other potentials only in the concentration of atomic hydrogen at the interface, and that no new processes begin at this potential as it is approached from either the positive or negative side. In other words, *there is nothing at all unique about the nature of processes occurring at the potential of the ordinary hydrogen electrode as distinct from the processes at potentials above or below this value.*

SUMMARY AND CONCLUSIONS

1. Reproducible current-cathode potential data have been obtained for platinized platinum electrodes in still and stirred solutions of 2 *N*

H₂SO₄ saturated in one case with hydrogen and in another with nitrogen at current densities from 2×10^{-6} to 1.3×10^{-2} amp./cm.² The cathode potential for a given current density is less negative in solutions saturated with nitrogen than in those saturated with hydrogen; it is also less negative in stirred solutions of both types than in still solutions.

2. In still solutions saturated with hydrogen there was a measurable overvoltage at the smallest current; in solutions stirred by hydrogen, however, there was no measurable overvoltage at currents less than 50 microamp.

3. Hydrogen has been formed at a platinized platinum cathode by the discharge of hydrogen ions at potentials appreciably more positive than the reversible value. In still solutions saturated with nitrogen a current of nearly 100 microamp. was needed to produce a polarized potential equal to the reversible value. In solutions stirred by nitrogen a current of more than one milliamper. was needed to produce an overvoltage potential.

4. In still and stirred solutions saturated with hydrogen and in still solutions saturated with nitrogen, the volt-log i curves were non-linear; in solutions stirred by nitrogen, however, the volt-log i curve was linear between potentials of + 0.06 and -0.03 volt, corresponding to currents, respectively, of 10^{-5} and 5×10^{-3} amp.

5. It has been found that prolonged use of an electrode at high currents under any of the conditions studied, or exposure to an atmosphere of hydrogen on open circuit, produces an "inactive" electrode with which reproducible data cannot afterward be obtained. Such an electrode may be reactivated by anodic polarization to evolve oxygen and subsequent cathodic polarization.

6. The modern theories of "activation" overvoltage and the much older Tafel theory are not consistent with the results of this research because none of them explain why the polarized potential at a particular current density depends on conditions existing in the body of the solution. Neither do they explain why considerable currents, anodic or cathodic, can flow in solutions stirred by hydrogen with no detectable displacement of the potential.

7. The theory presented affords a satisfactory explanation of the shapes of decomposition potential curves.

8. The results obtained support the theory that the potential of a hydrogen electrode is determined by the activity at the interface of hydrogen atoms and hydrogen ions, and that the primary factor in determining the activity of hydrogen atoms is the rate at which hydrogen may diffuse into, or away from, the interface.

ACKNOWLEDGMENT

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Resumen del artículo: "Estudios de Sobrevoltaje. XIV. Estudio del Potencial de Decomposición de Hidrógeno sobre Electrodos de Platino Platinizados bajo Condiciones Diversas en Soluciones Ácidas"

Es este estudio continuación de otros ya publicados. Resultados reproducibles de corriente-potencial catódico han sido obtenidos sobre electrodos de platino platinizado en soluciones 2 *N* de H_2SO_4 . La densidad de corriente usada vario entre 2×10^{-6} a 1.3×10^{-2} amp./cm.² El potencial catódico para cierta densidad de corriente fue menos negativo en soluciones saturadas con N_2 que con las con H_2 ; tambien fue menos negativo en soluciones agitadas de ambos tipos que en las calmas. Mientras en soluciones calmas saturadas con H_2 se pudo medir un sobrevoltaje con las corrientes mas bajas, esto no fue possible con menos de 50 microamperios en soluciones agitadas con H_2 , 100 micro amps. en solns. calmas saturadas con N_2 y 1 miliamperio en las soluciones agitadas con este último.

Solo fueron lineares las curvas volts-log *i* entre 0.06 y 0.030 voltios en soluciones agitadas con N_2 ; las otras no fueron lineares.

Se discuten las teorias de activación aplicandoles los datos obtenidos. Los resultados favorecen la teoria de que el potencial de un electrodo de hidrógeno esta determinado por la actividad de los átomos y de los iones en la región intermedia. La actividad de los átomos de H_2 debese principalmente a la razón con que el H_2 entra o sale de la región intermedia.

